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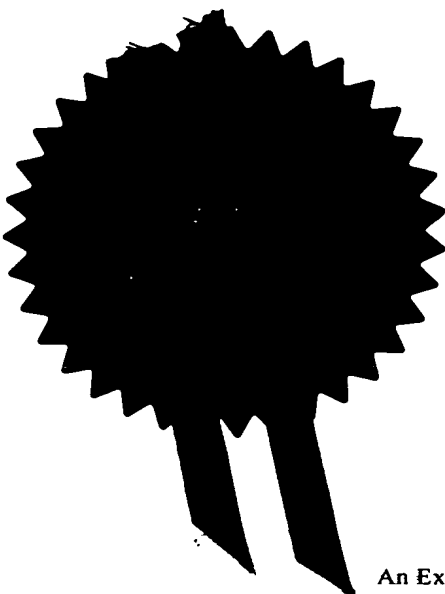
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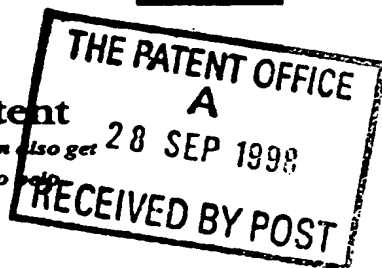
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Andrew Gersey

Dated 11 October 1999





Request for grant of a patent

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The Patent Office

Cardiff Road

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1. Your reference

APB/MER/P310

2. Patent application number

(The Patent Office will fill in this part)

28 SEP 1998

9820940.6

3. Full name, address and postcode of the or of each applicant (underline all surnames)

VICTREX MANUFACTURING LIMITED
Victrex Technology Centre
Hillhouse International
PO Box 4, Thornton Cleveleys
Lancashire, FY5 4QD

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

UK

6510887001

4. Title of the invention

SULPHONATED POLYMERS

5. Name of your agent (if you have one)

APPLEYARD LEES

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

15 CLARE ROAD
HALIFAX
WEST YORKSHIRE
HX1 2HY

190001

Patents ADP number (if you know it)

AA005

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number

Date of filing

(if you know it)

(day / month / year)

UK

9819706.4

11.09.98

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing

(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
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Yes

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description

Claim(s)

Abstract

Drawing(s)

26

6

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature

Date

A P Brierley

25.9.98

12. Name and daytime telephone number of person to contact in the United Kingdom

A P BRIERLEY
01422 330110

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Notes

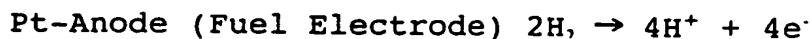
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SULPHONATED POLYMERS

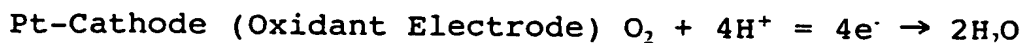
This invention relates to sulphonated polymers and particularly, although not exclusively, relates to sulphonated polyaryletherketones, polyarylethersulphones and/or copolymers of the aforesaid. Preferred embodiments of the invention relate to ion-conductive membranes, for example of polymer electrolyte membrane fuel cells, made using such polymers. The invention also relates to novel non-sulphonated polyaryletherketones and/or polyarylethersulphones used for preparing said sulphonated polymers and processes for the preparation of polymers described herein.

A polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the accompanying diagrammatic drawings, may comprise a thin sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than 1mm thickness.

In a PEMFC, hydrogen is introduced at the anode (fuel electrode) which results in the following electrochemical reaction:



The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at the cathode (oxidant electrode) where the following electrochemical reaction takes place:



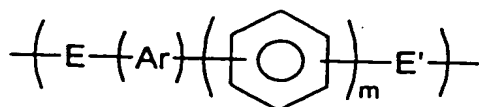
Thus, electrons and protons are consumed to produce water and heat. Connecting the two electrodes through an external circuit causes an electrical current to flow in the circuit and withdraw electrical power from the cell.

US Patent No. 5 561 202 (Hoechst) discloses the production of PEMs from sulphonated aromatic polyether ketones. At least 5% of the sulphonic groups in the sulphonic acid moieties are converted into sulphonyl chloride groups and then reacted with an amine containing at least one cross-linkable substituent or a further functional group. An aromatic sulphonamide is then isolated, dissolved in an organic solvent, converted into a film and then the cross-linkable substituents in the film are cross-linked. The invention is said to provide ion-conductive membranes suitable for use as polymeric solid electrolytes which have adequate chemical stability and can be produced from polymers which are soluble in suitable solvents.

One problem associated with known PEMFCs is that of providing PEMs which have desirable properties at elevated temperatures and which are cheap to manufacture.

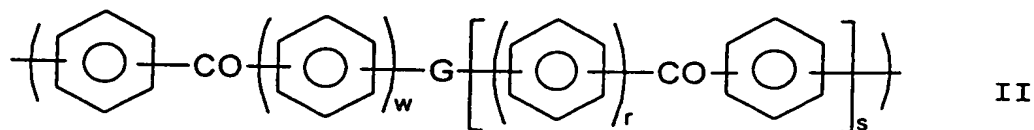
It is an object of the present invention to address problems associated with PEMs.

According to a first aspect of the invention, there is provided a polymer electrolyte membrane which includes a polymer having a moiety of formula

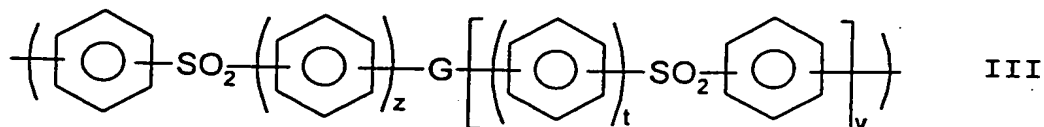


I

and/or a moiety of formula

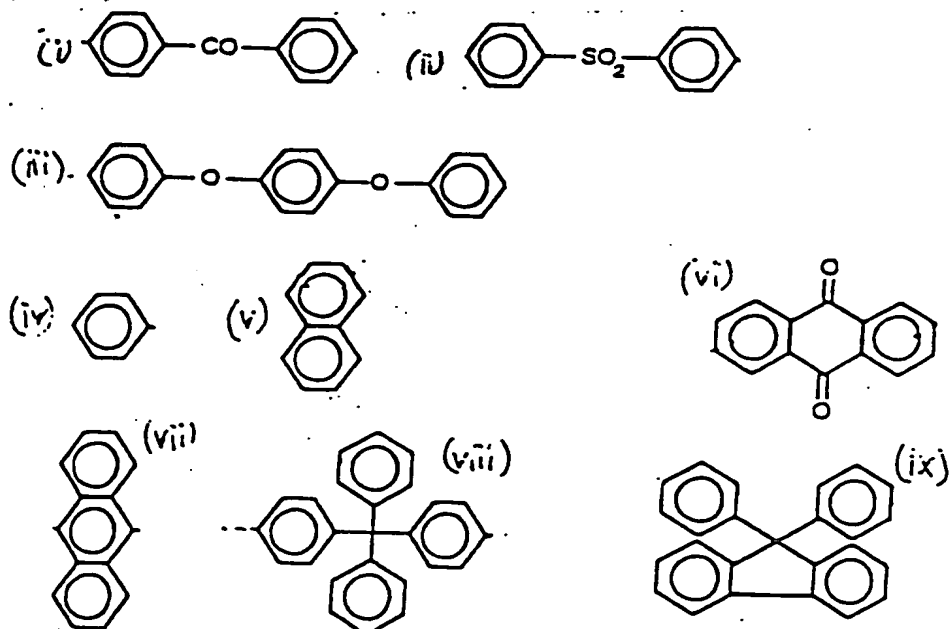


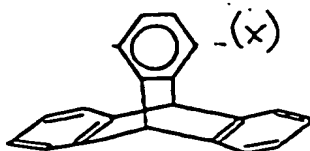
5 and/or a moiety of formula



10

wherein at least some of the units I, II and/or III are sulphonated; wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from one of the following moieties (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties





Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to moieties to which it is bonded.

Said polymer may include more than one different type of repeat unit of formula I; more than one different type of repeat unit of formula II; and more than one different type of repeat unit of formula III.

Where the phenyl moieties in units I, II or III are optionally substituted, they may be optionally substituted by one or more halogen, especially fluorine and chlorine, atoms or alkyl, cycloalkyl or phenyl groups. Preferred alkyl groups are C_{1-10} , especially C_{1-4} , alkyl groups. Preferred cycloalkyl groups include cyclohexyl and multicyclic groups, for example adamantyl. In some cases, the optional substituents may be used in the cross-linking of the polymer. For example, hydrocarbon optional substituents may be functionalised, for example sulphonated, to allow a cross-linking reaction to take place. Preferably, said phenyl moieties are unsubstituted.

Where said polymer is cross-linked, it is suitably cross-linked so as to improve its properties as a polymer electrolyte membrane, for example to reduce its swellability in water. Any suitable means may be used to effect cross-linking. For example, where E represents a sulphur atom, cross-linking between polymer chains may be

effected via sulphur atoms on respective chains. Alternatively, said polymer may be cross-linked via sulphonamide bridges as described in US 5 561 202. A further alternative is to effect cross-linking as described in EP-A-0008895.

However, for polymers according to the first aspect which are crystalline (which some are) there may be no need to effect cross-linking to produce a material which can be used as a polymer electrolyte membrane. Such polymers may be easier to prepare than cross-linked polymers. Thus, said polymer of the first aspect is preferably crystalline. Preferably, said polymer is not optionally cross-linked as described.

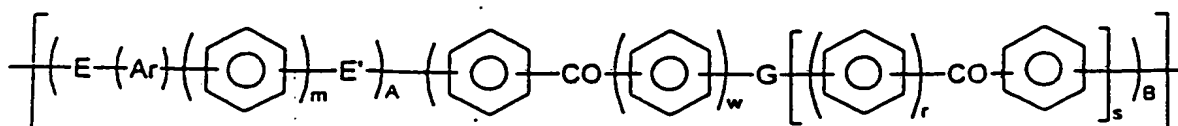
Where w and/or z is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, said phenylene moieties have 1,4- linkages.

Preferably, G represents a direct link.

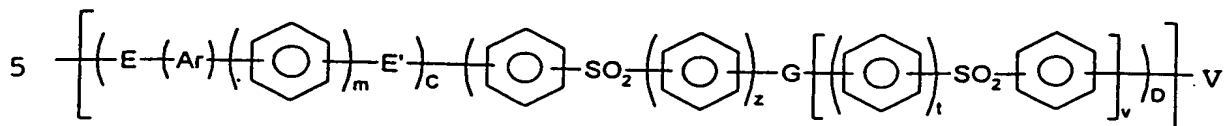
Suitably, "a" represents the mole % of units of formula I in said polymer; "b" represents the mole % of units of formula II in said polymer; and "c" represents the mole % of units of formula III in said polymer. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52. Preferably, the sum of b and c is in the range 0-55, more preferably in the range 45-55, especially in the range 48-52. Preferably, the sum of a, b and c is 100.

Said polymer may be a homopolymer having a repeat unit of general formula

IV



or a homopolymer having a repeat unit of general formula



or a random or block copolymer of at least two different units of IV and/or V

10

wherein A, B, C and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

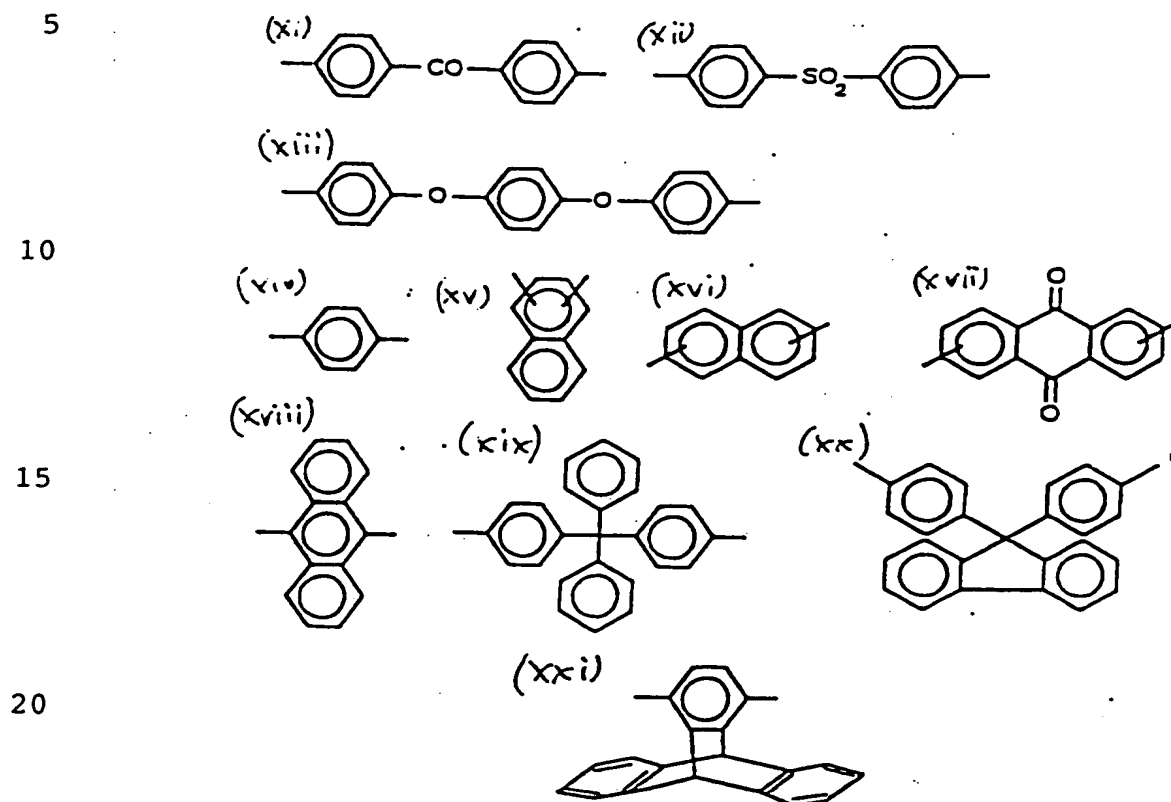
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Preferably, m is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably t is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, s is 0 or 1. Preferably v is 0 or 1.

20

Preferably, w is 0 or 1. Preferably z is 0 or 1.

Preferably Ar is selected from the following moieties (xi) to (xxi):



25 Preferably, (xv) is selected from a 1,2-, 1,3-, or a 1,5- moiety; (xvi) is selected from a 1,6-, 2,3-, 2,6- or a 2,7- moiety; and (xvii) is selected from a 1,2-, 1,4-, 1,5-, 1,8- or a 2,6- moiety.

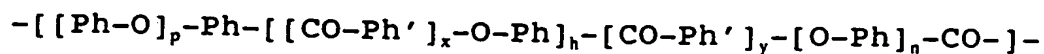
30 Referring to formula IV, preferably, said polymer is not a polymer wherein: Ar represents moiety (iv), E and E' represent oxygen atoms, m represents zero, w represents 1, s represents zero, and A and B represent 1; Ar represents moiety (i), E and E' represent oxygen atoms, G represents

35 a direct link, m represents zero, w represents 1, r

represents 0, s represents 1 and A and B represent 1; Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents 0, w represents 0, s represents 1, r represents 1 and A and B represent 1.

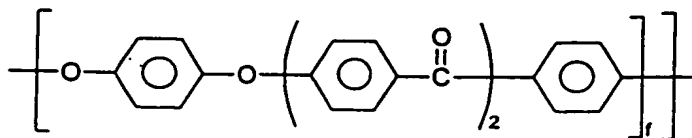
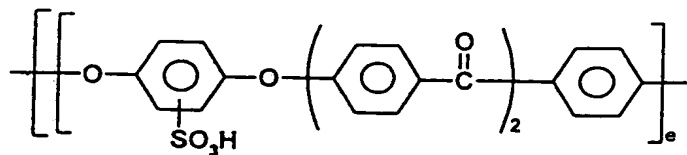
5 Referring to formula V, preferably Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents zero, z represents 1, v represents zero and C and D represent 1.

10 Preferably, said polymer is not a sulphonated aromatic polyetherketone of formula



15 where Ph represents a 1,4- or 1,3- phenylene moiety; Ph' represents phenylene, naphthylene, biphenylene or anthrylene; p is 1, 2, 3 or 4; x, h and n are, independently, zero or 1; and y is 1, 2 or 3.

20 Preferably, said polymer does not conform to the formula



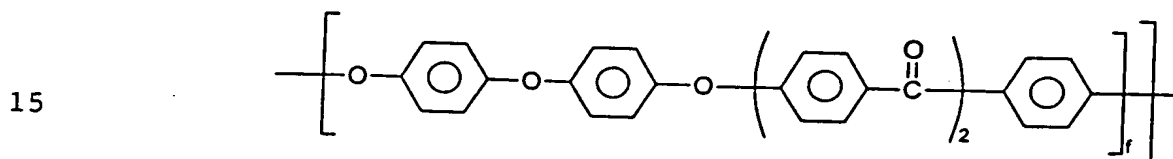
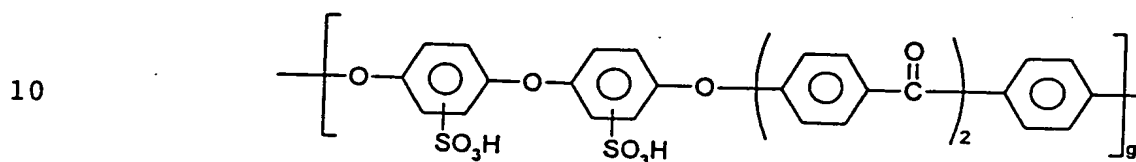
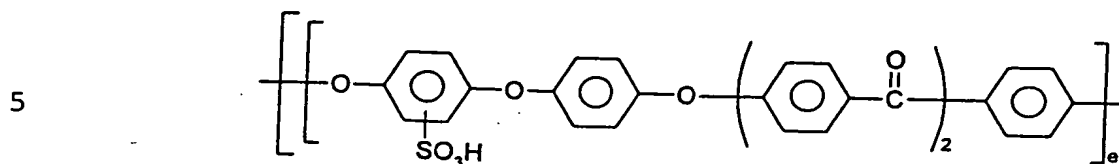
where

e is from 0.2 to 1,

f is from 0 to 0.8, and

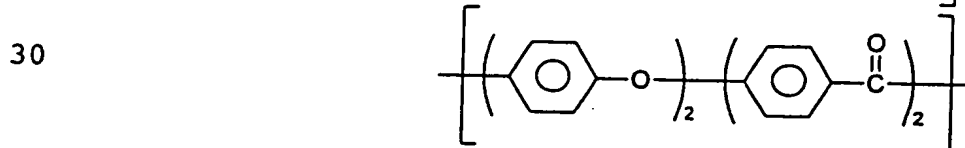
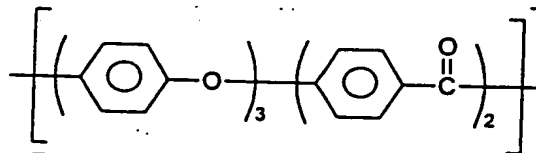
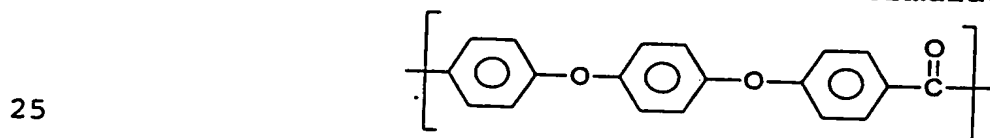
e + f = 1

Preferably, said polymer does not conform to the formula



in which e is a number from 0 to 1, g is a number from 0 to 1, f is a number from 0 to 0.5, and the sum $e + f + g = 1$.

Preferably, said polymer is not a copolymer built up from at least two different units of formulae:



Preferred moieties Ar are moieties (i), (ii) and (v), especially moieties (xi), (xii), (xv) and (xvi).

Preferred polymers include a biphenylene moiety.
Preferred polymers include a -O-biphenylene-O- moiety.

Preferred polymers are copolymers comprising a first
5 repeat unit which is either:

(a) of formula IV wherein E and E' represent oxygen
atoms, G represents a direct link, Ar represents a moiety
of structure (iv), m and s represent zero, w represents 1
10 and A and B represent 1; or

(b) of formula IV wherein E represents an oxygen
atom, E' represents a direct link, Ar represents a moiety
of structure (i), m represents zero, A represents 1, B
15 represents zero;

and a second repeat unit which is either:

(c) of formula IV wherein E and E' represent oxygen
20 atoms, G represents a direct link, Ar represents a moiety
of structure (iv), m represents 1, w represents 1, s
represents zero, A and B represent 1; or

(d) of formula IV wherein E represents an oxygen
25 atom, E' is a direct link, G represents a direct link, Ar
represents a moiety of structure (iv), m and s represent
zero, w represent 1, A and B represent 1.

Especially preferred polymers are copolymers having
30 a first repeat unit as described in paragraph (a) or (b)
in combination with a repeat unit as described in
paragraph (c).

Where a phenyl moiety is sulphonated, it may only be
35 mono-sulphonated.

Where a said polymer includes a -O-phenyl-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. Where a said polymer includes a -O-biphenylene-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. 5 More generally, it is believed to be possible to sulphonate -O-(phenyl)_n-O- moieties wherein n is an integer, suitably 1-3, at up to 100 mole%. Moieties of formula -O-(phenyl)_n-CO- or -O-(phenyl)_n-SO₂- may also be sulphonated at up to 100 mole%. Moieties of formulae 10 -CO-(phenyl)_n-CO- and -SO₂-(phenyl)_n-SO₂- are more difficult to sulphonate and may be sulphonated to a level less than 100 mole%.

The glass transition temperature (T_g) of said polymer 15 may be at least 154°C, preferably at least 170°C, more preferably at least 190°C. In some cases, the T_g may be greater than 250°C or even 300°C.

Said polymer may have an inherent viscosity (IV) of 20 at least 0.4, preferably at least 0.7 (which corresponds to a reduced viscosity (RV) of least 0.8) wherein RV is measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84gcm³, said solution containing 1g of polymer per 100cm³ of solution. 25 IV is measured at 25°C on a solution of polymer in concentrated sulphuric acid of density 1.84gcm³, said solution containing 0.1g of polymer per 100cm³ of solution.

The measurements of both RV and IV both suitably 30 employ a viscometer having a solvent flow time of approximately 2 minutes.

The main peak of the melting endotherm (T_m) for said polymer (if crystalline) may be at least 300°C.

In general terms, said polymer is preferably substantially stable when used as a PEM in a fuel cell. Thus, it suitably has high resistance to oxidation, reduction and hydrolysis and has very low permeability to reactants in the fuel cell. Preferably, however, it has a high proton conductivity. Furthermore, it suitably has high mechanical strength and is capable of being bonded to other components which make up a membrane electrode assembly.

Said polymer may comprise a film, suitably having a thickness of less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05 mm. The film may have a thickness of at least 5 μ m.

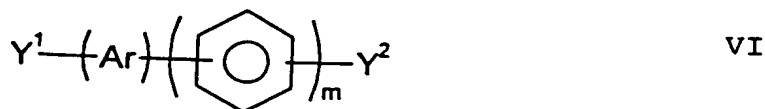
The polymer electrolyte membrane suitably includes a layer of a catalyst material, which may be a platinum catalyst or a mixture of platinum and ruthenium, on both sides of the polymer film. Electrodes may be provided outside the catalyst material.

According to a second aspect of the invention, there is provided a fuel cell incorporating a polymer electrolyte membrane according to the first aspect.

According to a third aspect of the invention, there is provided any novel polymer as described according to said first aspect per se.

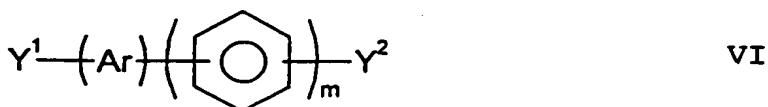
According to a fourth aspect of the invention, there is provided a process for the preparation of a polymer as described in the first, second and/or third aspects, the process comprising:

(a) polycondensing a compound of general formula



with itself wherein Y^1 represents a halogen atom or a group $-EH$ and Y^2 represents a halogen atom or, if Y^1 represents a halogen atom, Y^2 represents a group $E'H$; or

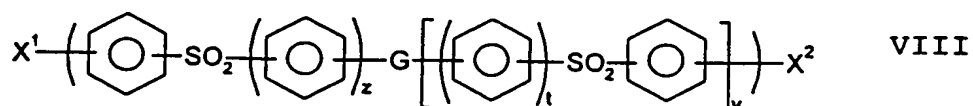
(b) polycondensing a compound of general formula



with a compound of formula



and/or with a compound of formula



wherein Y^1 represents a halogen atom or a group $-EH$ (or $-E'H$ if appropriate) and X^1 represents the other one of a halogen atom or group $-EH$ (or $-E'H$ if appropriate) and Y^2 represents a halogen atom or a group $-E'H$ and X^2 represents the other one of a halogen atom or a group $-E'H$ (or $-EH$ if appropriate).

(c) optionally copolymerizing a product of a process as described in paragraph (a) with a product of a process as described in paragraph (b);

5 wherein the phenyl moieties of units VI, VII and/or VIII are optionally substituted; the compounds VI, VII and/or VIII are optionally sulphonated; and Ar, m, w, r, s, z, t, v, G, E and E' are as described above except that E and E' do not represent a direct link;

10 the process also optionally comprising sulphonating and/or cross-linking a product of the reaction described in paragraphs (a), (b) and/or (c) to prepare said polymer.

15 Preferably, where Y¹, Y², X¹ and/or X² represent a halogen, especially a fluorine, atom, an activating group, especially a carbonyl or sulphone group, is arranged ortho- or para- to the halogen atom.

20 Advantageously, where it is desired to prepare a copolymer comprising a first repeat unit IV or V wherein E represent an oxygen or sulphur atom, Ar represents a moiety of structure (i), m represents zero, E' represents a direct link, A represents 1 and B represents zero and
25 a second repeat unit IV or V wherein E and E' represent an oxygen or sulphur atom, Ar represents a moiety of structure (iv), m and w represent 1, G represents a direct link, s represents zero and A and B represent 1 wherein the polymer is not a random polymer but has a regular
30 structure, the process described in paragraph (b) above may be used wherein in said compound of general formula VI, Y¹ and Y² represent -OH or -SH groups, Ar represents a moiety of structure (iv) and m represents 1 and in said compounds of general formulae VII and VIII, X¹ and X²

represent a fluorine atom, w,r,s,z,t and v represent 1 and G represents an oxygen or sulphur atom.

5 In another embodiment, where it is desired to prepare a copolymer comprising a first repeat unit IV or V wherein E and E' represent an oxygen or sulphur atom, Ar represents a moiety of structure (iv), m represents zero, A represents 1, w represents 1, s represents zero and B represents 1 and a second repeat unit IV or V wherein E and E' represent an oxygen or sulphur atom, Ar represents a moiety of structure (iv), m and w represent 1, s represents zero and A and B represent 1, wherein the polymer is not a random polymer but has a regular structure, the process described in paragraph (b) above may be used wherein in said compound of general formula VI, Y¹ and Y² represent -OH or -SH groups, Ar represents a moiety of structure (iv) and m represents 1 and in said compounds of general formulae VII and VIII, X¹ and X² represent a fluorine atom, w,r,s,z,t and v represent 1 and G represents a -O-Ph-O- moiety.

Preferred halogen atoms are fluorine and chlorine atoms, with fluorine atoms being especially preferred. Preferably, halogen atoms are arranged meta- or para- to activating groups, especially carbonyl groups.

Where the process described in paragraph (a) is carried out, preferably one of Y¹ and Y² represents a fluorine atom and the other represents an hydroxy group. More preferably in this case, Y¹ represents a fluorine atom and Y² represents an hydroxy group. Advantageously, the process described in paragraph (a) may be used when Ar represents a moiety of structure (i) and m represents 1.

When a process described in paragraph (b) is carried out, preferably, Y¹ and Y² each represent an hydroxy group. Preferably, X¹ and X² each represent a halogen atom, suitably the same halogen atom.

5

Compounds of general formula VI, VII and VIII are commercially available (eg from Aldrich U.K.) and/or may be prepared by standard techniques, generally involving Friedel-Crafts reactions, followed by appropriate derivatisation of functional groups. The preparations of some of the monomers described herein are described in P M Hergenrother, B J Jensen and S J Havens, Polymer 29, 358 (1988), H R Kricheldorf and U Delius, Macromolecules 22, 517 (1989) and P A Staniland, Bull, Soc, Chem, Belg., 98 (9-10), 667 (1989).

15

Where compounds VI, VII and/or VIII are sulphonated, compounds of formulas VI, VII and/or VIII which are not sulphonated may be prepared and such compounds may be sulphonated prior to said polycondensation reaction.

20

Sulphonation as described herein may be carried out in concentrated sulphuric acid (96%w/w) at an elevated temperature. For example, dried polymer may be contacted with sulphuric acid and heated with stirring at a temperature of greater than 40°C, preferably greater than 55°C, for at least one hour, preferably at least two hours, more preferably about three hours. The desired product may be caused to precipitate, suitably by contact with cooled water, and isolated by standard techniques. Sulphonation may also be effected as described in US5362836 and/or EP0041780.

25

30

Where the process described in paragraph (b) is carried out, suitably, "a*" represents the mole% of

35

compound VI used in the process; "b*" represents the mole % of compound VII used in the process; and "c*" represents the mole % of compound VIII used in the process.

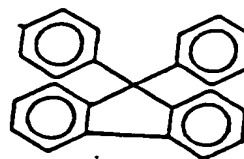
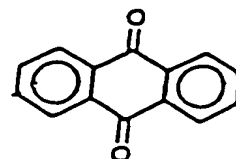
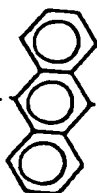
5 Preferably, a* is in the range 45-55, especially in the range 48-52. Preferably, the sum of b* and c* is in the range 45-55, especially in the range 48-52. Preferably, the sum of a*, b* and c* is 100.

10 Where the process described in paragraph (b) is carried out, preferably, one of either the total mole % of halogen atoms or groups -EH/-E'H in compounds VI, VII and VIII is greater, for example by up to 10%, especially up to 5%, than the total mole % of the other one of either
15 the total mole % of halogen atoms or groups -EH/-E'H in compounds VI, VII and VIII. Where the mole % of halogen atoms is greater, the polymer may have halogen end groups and be more stable than when the mole % of groups -EH/-E'H is greater in which case the polymer will have -EH/-E'H
20 end groups. However, polymers having -EH/-E'H end groups may be advantageously cross-linked.

 It is believed that certain polymers described herein are novel and, therefore, in a fifth aspect, the invention
25 extends to any novel polymer described herein per se.

 It is also believed that certain polymers according to said first aspect but which are not sulphonated are novel. Thus, according to a sixth aspect of the
30 invention, there is provided a novel polymer having a moiety of formula I and/or a moiety of formula II and/or a moiety of formula III wherein E, E', G, m, r, s, t, v, w, z and Ar are as described in any statement herein.

Preferably, said polymer includes a moiety of formula II and/or III and Ar is selected from



Preferably, in the aforementioned formulae, each -Ar- is bonded to adjacent moieties as described in any statement herein.

20

According to a seventh aspect of the invention, there is provided a process for the preparation of novel polymers according to said sixth aspect, the process being as described according to the process of the fourth aspect

25

except that compounds VI, VII and VIII are not sulphonated and the process does not include a sulphonation step.

Sulphonated polymers described herein may be made into films and/or membranes for use as PEMs by

30

conventional techniques, for example as described in Examples 5 to 7 of US 5561202.

Any feature of any aspect of any invention or example described herein may be combined with any feature of any

35

aspect of any other invention or example described herein.

Specific embodiments of the invention will now be described, by way of example, with reference to figure 1 which is a schematic representation of a polymer electrolyte membrane fuel cell.

5

As described above, the fuel cell includes a thin sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane. The preparation of sheet material for such a membrane is described hereinafter.

10

Example 1

A 500ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with
15 4,4'-difluorobenzophenone (35.79g, 0.164 mole), hydroquinone (11.01g, 0.10 mole), 4,4'-dihydroxybiphenyl (18.62g, 0.10 mole), 4,4'-bis(4-chlorophenylsulphonyl)biphenyl (LCDC)(20.13g, 0.04 mole) and diphenylsulphone (202.76g) and the contents were
20 heated under a nitrogen blanket to 160°C to form a nearly colourless solution. While maintaining a nitrogen blanket, anhydrous potassium carbonate (29.02g, 0.21 mole) was added and the mixture stirred for 35 minutes. The temperature was raised gradually to 220°C over 2 hours then
25 raised to 280°C over 2 hours and maintained for 2 hours.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer
30 had a reduced viscosity of (RV) 2.50 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm⁻³, said solution containing 1g of polymer/100cm³) and a Tg of 186°C.

35

Example 2

A 250ml, 3-necked round-bottomed flask fitted with stirrer, nitrogen inlet and air condenser was charged with
5 4,4'-difluorobenzophenone (33.06g, 0.1515 mole), hydroquinone (13.21g, 0.12 mole), 9,9'-bis(4-hydroxyphenyl)fluorene(HPF) (10.512g, 0.03 mole), and diphenylsulphone (100.93g) and the contents were heated under a nitrogen blanket to 150°C to form a nearly
10 colourless solution. While maintaining a nitrogen blanket, anhydrous potassium carbonate (21.77g, 0.15751 mole) was added. The temperature was raised to 175°C maintained for 2 hours, raised to 200°C maintained for 50 minutes, raised to 250°C maintained for 45 minutes, raised
15 to 300°C maintained for 90 minutes.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer
20 had an reduced viscosity (RV) of 0.76 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm⁻³, said solution containing 1g of polymer/100cm³) and a Tg of 165°C.

25 **Example 3**

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with
30 4,4'-difluorobenzophenone (11.36g, 0.052 mole), 4,4'-dihydroxybenzophenone (21.42g, 0.10 mole), LCDC (25.72g, 0.05 mole), and diphenylsulphone (90g) and the contents were heated under a nitrogen blanket to 155°C to form a nearly colourless solution. While maintaining a nitrogen blanket, anhydrous sodium carbonate (10.60g, 0.10 mole)
35 and potassium carbonate (0.28g, 0.002 mole) was added.

The temperature was raised to 180°C and maintained for 20 minutes, raised to 200°C and maintained for 1 hour, raised to 250°C and maintained for 30 minutes, raised to 275°C and maintained for 20 minutes, raised to 300°C and maintained for 20 minutes, raised to 325°C and maintained for 2 hours.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had a Tg of 200°C.

Example 4

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-bis(4-chlorophenylsulphonyl)-terphenyl (23.2g, 0.04 mole), 4,4'-dihydroxybiphenyl (7.44g, 0.040 mole) and diphenylsulphone (80g) and the contents were heated under a nitrogen blanket to 170°C to form a nearly colourless solution. While maintaining a nitrogen blanket, anhydrous potassium carbonate (5.64g, 0.408 mole) was added. The temperature was raised to 200°C and maintained for 30 minutes, raised to 250°C and maintained for 15 minutes, raised to 275°C and maintained for 15 minutes, raised to 330°C and maintained for 1 hour.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had an inherent viscosity (IV) of 0.50 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm⁻³, said solution containing 0.1g of polymer/100cm³) and a Tg of 264°C.

Example 5

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with
5 4,4'-difluorobenzophenone (21.82g, 0.10 mole), 4,4'-
dihydroxybiphenyl (18.62g, 0.10 mole) and diphenylsulphone
(60g) and the contents were heated under a nitrogen
blanket to 180°C to form a nearly colourless solution.
While maintaining a nitrogen blanket anhydrous potassium
10 carbonate (14.10g, 0.102 mole) was added. The temperature
was raised to 200°C over 60 minutes, raised to 250°C
maintained for 5 mins, raised to 325°C maintained for 5
mins, raised to 370°C over 90 mins, maintained for 10 mins.

15 The reaction mixture was allowed to cool, milled and
washed with acetone/methanol and water. The resulting
solid polymer was dried at 140°C under vacuum. The polymer
had an inherent viscosity (RV) of 1.28 (measured at 25°C on
a solution of the polymer in concentrated sulphuric acid
20 of density 1.84g.cm³, said solution containing 1g of
polymer/100cm³) and a Tg 167°C.

Example 6

25 A 250ml, 3-necked round-bottomed flask fitted with a
stirrer, nitrogen inlet and air condenser was charged with
4,4'-difluorobenzophenone (22.04g, 0.101 mole), 4,4'-
dihydroxybiphenyl (6.52g, 0.035 mole), hydroquinone
(7.16g, 0.065 mole) and diphenylsulphone (60g) and the
30 contents were heated under a nitrogen blanket to 180°C to
form a nearly colourless solution. While maintaining a
nitrogen blanket anhydrous sodium carbonate (10.60g, 0.100
mole) and anhydrous potassium carbonate (0.28g, 0.002
mole) were added. The temperature was raised to 200°C held
35 for 1 hour, raised to 250°C held for 1 hour, raised to

300°C held for 1 hour. The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer has an inherent viscosity (IV) 0.92 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84 g.cm⁻³, said solution containing 0.1 g of polymer/100cm³) and a T_g 156°C.

Example 7

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-bis(4-fluorobenzoyl)diphenylether (21.34g, 0.515 mole), 4,4'-dihydroxybiphenyl (9.31g, 0.050 mole) and diphenylsulphone (90g) and the contents were heated under a nitrogen blanket to 160°C to form a nearly colourless solution. While maintaining a nitrogen blanket anhydrous sodium carbonate (5.30g, 0.050 mole) and anhydrous potassium carbonate (0.14g, 0.001 mole) were added. The temperature was raised at 1°C/min until it reached 345°C and held for 1 hour.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had an inherent viscosity (RV) 1.48 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm⁻³, said solution containing 1g of polymer/100cm³) and a T_g 163°C.

Example 8 - General procedur for Sulphonation of
Polymers of Examples 1 to 7

5 The polymers prepared as described in Examples 1 to
7 were sulphonated according to the following procedure.

10 The dried polymer was placed in a three-necked round-
bottomed flask fitted with a stirrer containing 98%
concentrated sulphuric acid (100cm³), heated with stirring
to 60°C and maintained at the temperature for 3 hours. The
reaction product was poured into 5 litres of stirred
ice/water mixture. The product precipitated out. It was
then filtered-off, washed with iced-water until the pH was
neutral, washed with methanol and dried under vacuum at
15 100°C. The degree of sulphonation was determined by
elemental analysis, filtration or Nmr.

Example 9 - Sulphonation of polymer of Example 6
(Process 1)

20

The dried polymer from Example 6 (10g) was placed in
a three-necked round-bottomed flask fitted with a stirrer,
containing 98% concentrated sulphuric acid (100cm³), heated
with stirring to 60°C and maintained at that temperature
25 for 3 hours. The reaction products was poured into 5
litres of stirred ice/water mixture. The product
precipitated out, was filtered-off, washed with iced-water
until the pH was neutral, washed with methanol and dried
under vacuum at 100°C. Nmr analysis showed the polymer had
30 readily sulphonated, in which 95-100 mole% of the ether-
diphenyl-ether and ether-phenyl-ether units had been
sulphonated.

Example 10 - Sulphonation of polymer of Example 6
(Process 2)

5 The dried polymer from Example 6 (10g) was placed in
a three-necked round-bottomed flask fitted with a stirrer,
containing 96% concentrated sulphuric acid (100cm³) and
stirred for 90 minutes at 60°C until the polymer was
completely dissolved. Oleum was added to bring the
sulphuric acid concentration up to 98.5%. The mixture was
10 heated with stirring to 80°C and maintained at that
temperature for 3 hours. The reaction product was poured
into 5 litres of stirred ice/water mixture. The product
precipitated out, was filtered-off, washed with iced-water
until the pH was neutral, washed with methanol and dried
15 under vacuum at 100°C. Nmr analysis showed the polymer had
readily sulphonated, in which 100 mole% of the ether-
diphenyl-ether and ether-phenyl-ether units and 26 mole%
of the ether-phenyl-ketone units had been sulphonated.

20 The reader's attention is directed to all papers and
documents which are filed concurrently with or previous to
this specification in connection with this application and
which are open to public inspection with this
specification, and the contents of all such papers and
25 documents are incorporated herein by reference.

All of the features disclosed in this specification
(including any accompanying claims, abstract and
drawings), and/or all of the steps of any method or
30 process so disclosed, may be combined in any combination,
except combinations where at least some of such features
and/or steps are mutually exclusive.

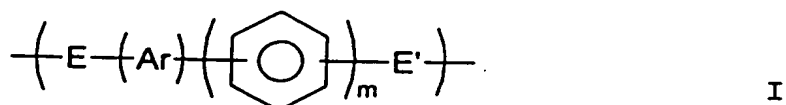
Each feature disclosed in this specification
35 (including any accompanying claims, abstract and

drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of
5 a generic series of equivalent or similar features.

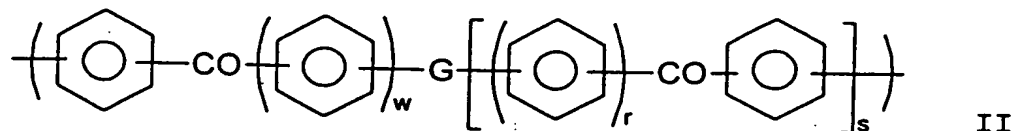
The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features
10 disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

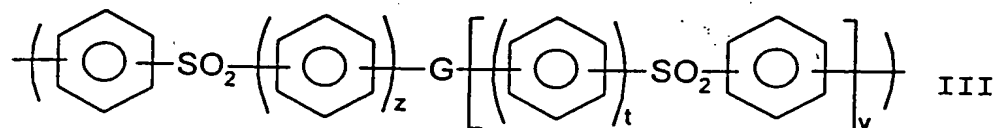
1. A polymer electrolyte membrane which includes a polymer having a moiety of formula



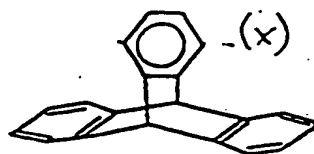
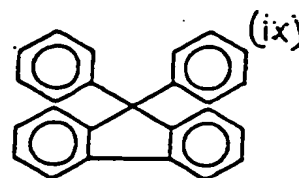
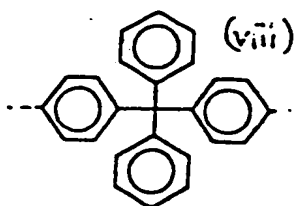
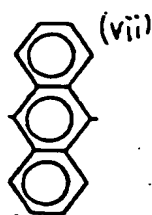
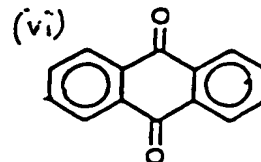
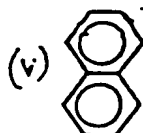
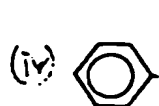
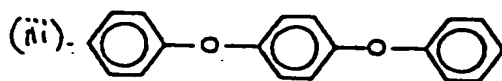
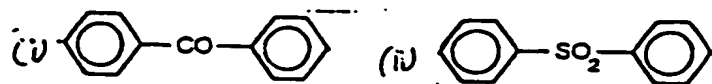
and/or a moiety of formula



and/or a moiety of formula

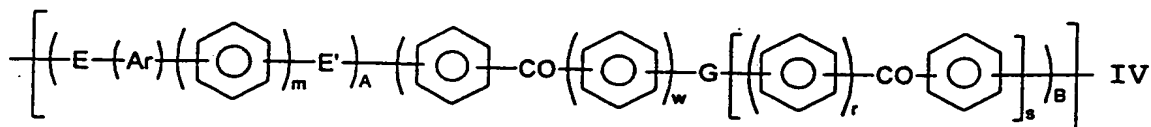


wherein at least some of the units I, II and/or III are sulphonated; wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from one of the following moieties (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties

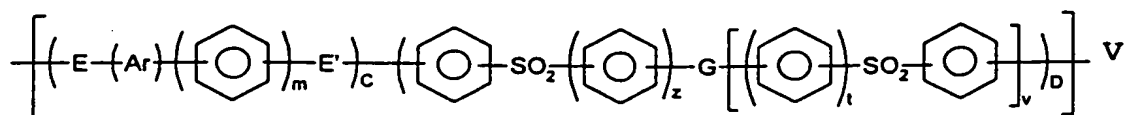


2. A membrane according to claim 1, wherein "a" represents the mole % of units of formula I in said polymer; "b" represents the mole % of units of formula II in said polymer; and "c" represents the mole % of units of formula III in said polymer and wherein a is in the range 45-100 and the sum of b and c is in the range 0-55.

3. A membrane according to claim 1 or claim 2, wherein said polymer is a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula



5 or a random or block copolymer of at least two different units of IV and/or V

wherein A, B, C and D independently represent 0 or 1.

10 4. A membrane according to claim 3, wherein said polymer is a copolymer comprising a first repeat unit which is either:

15 (a) of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1; or

20 (b) of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

25 and a second repeat unit which is either:

30 (c) of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1; or

35 (d) of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1.

5. A membrane according to claim 4, wherein said polymer has a repeat unit as described in paragraph (a) or (b) in combination with a repeat unit as described in paragraph (c).

5

6. A membrane according to any preceding claim, wherein said polymer includes a biphenylene moiety.

7. A membrane according to any preceding claim, wherein said polymer includes a -O-biphenylene-O- moiety.

10

8. A membrane according to any preceding claim, wherein said polymer has a glass transition temperature (T_g) of at least 154°C.

15

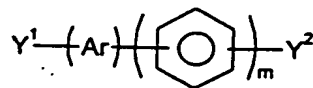
9. A fuel cell incorporating a polymer electrolyte membrane according to any preceding claim.

10. A novel polymer as described in any of claims 1 to 8 per se.

20

11. A process for the preparation of a polymer according to any of claims 1 to 8, the process comprising:

25 (a) polycondensing a compound of general formula

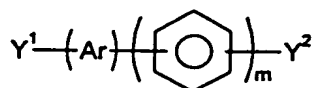


VI

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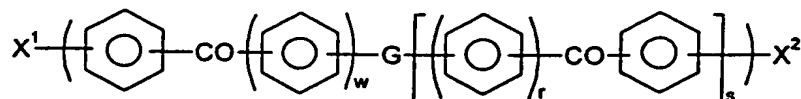
with itself wherein Y¹ represents a halogen atom or a group -EH and Y² represents a halogen atom or, if Y¹ represents a halogen atom, Y² represents a group E'H; or

35 (b) polycondensing a compound of general formula



VI

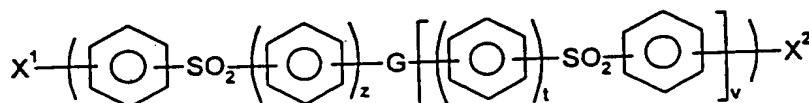
5 with a compound of formula



VII

10

and/or with a compound of formula



VIII

15

wherein Y^1 represents a halogen atom or a group $-EH$ (or $-E'H$ if appropriate) and Y^2 represents a halogen atom or a group $-E'H$ and X^2 represents the other one of a halogen atom or a group $-E'H$ (or $-EH$ if appropriate; and

(c) optionally copolymerizing a product of a process as described in paragraph (a) with a product of a process as described in paragraph (b);

25

wherein the phenyl moieties of units VI, VII and/or VIII are optionally substituted; the compounds VI, VII and/or VIII are optionally sulphonated; and Ar, m, w, r, s, z, t, v, G, E and E' are as described in any of claims 1 to 8 except that E and E' do not represent a direct link; the process also optionally comprising sulphonating and/or cross-linking a product of the reaction described in paragraphs (a), (b) and/or (c) to prepare said polymer.

35

12. A novel polymer as described in any of claims 1 to 8
(except that the polymer is not sulphonated) *per se*.

5 13. A membrane, a fuel cell, a process, a novel polymer,
each being independently substantially as hereinbefore
described, with reference to the examples.

10

15